JAPANESE / ENGLISH TRANSLATION OF

Japanese Patent Application JP 7 - 60924 A

Multilayered Polyester Sheet

Your Ref: 102203 - 19

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(19) Japanese Patent Office (JP)

(11) Unexamined Patent Application No:
7-60924

(12) Unexamined Patent Gazette (A)

(43) Date of Publication: March 7, 1995

(51) Int. Cl.[6]		Class. Symbols	Internal Office Registration Nos.:	FI	Technical Classification Field
B32B	27/36		7421-4F		
//B29C	51/00		7421-4F		
B29K	67:00				

Request for Examination: Not yet submitted   Number of Claims: 5 OL   (Total of 7 pages [in the original])

(21) Application No.: Hei 5-212705

(22) Date of Filing: August 27, 1993

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(54) [Title of the Invention] Multilayered Polyester Sheet

(57) [Summary]

[Object] To obtain an amorphous polyester resin sheet with good antistatic properties and excellent transparency.

[Means of Achievement] A multilayered sheet is obtained by means of forming surface layers comprising a composition that contains 0.05 to 2 parts by weight glycerin fatty acid ester per 100 parts by weight polyester resin on both surfaces of a transparent polyester resin base layer. This sheet is obtained as an unstretched sheet or a sheet with a low draw ratio.

[Effect] The surface layers contain a glycerin fatty acid ester that has a potent effect as an antistatic agent, thereby yielding an excellent antistatic property without any loss in transparency.

[Claims]

[Claim 1] A multilayered polyester sheet obtained by means of forming surface layers comprising a composition that contains 0.05 to 2 parts by weight glycerin fatty acid ester per 100 parts by weight polyester resin on both surfaces of a transparent polyester resin base layer.

[Claim 2] The multilayered polyester sheet of Claim 1, wherein the polyester resin on both surfaces principally consists of either an amorphous copolyester resin comprising a residue of a dicarboxylic acid composed mainly of terephthalic acid and a residue of a diol that contains 20 to 60 mol% 1,4-cyclohexane dimethanol, with the remainder being ethylene glycol, or of an amorphous copolyester resin comprising a residue of a dicarboxylic acid that contains 20 to 40 mol% isophthalic acid, with the remainder being terephthalic acid, and a residue of a diol composed mainly of ethylene glycol.

[Claim 3] The multilayered polyester sheet of Claims 1 or 2, wherein the surface layers contain 0.05 to 0.5 parts by weight of inert particles with a mean particle diameter of 2 to 10 μm per 100 parts by weight polyester resin.

[Claim 4] The multilayered polyester sheet of Claims 1, 2, or 3, wherein both surface layers are each 5 to 50 μm thick.

[Claim 5] A multilayered polyester sheet obtained by means of stretching in at least one direction, and at a ratio of 1.05 to 2, a substantially unoriented multilayered polyester sheet obtained by means of forming surface layers comprising a composition that contains 0.05 to 2 parts by weight glycerin fatty acid ester and 0.05 to 0.5 parts by weight of inert particles with a mean particle diameter of 2 to 10 μm per 100 parts by weight polyester resin on both surfaces of a transparent polyester resin base layer.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a multilayered polyester sheet to be cut and folded into a desired shape in order to obtain case-shaped articles; to obtain blisters or containers by means of vacuum molding or other thermoforming methods; or to be used in other applications.

[0002]

[Prior Art] Unstretched amorphous polyethylene terephthalate (PET) sheet is suitable for use as transparent cases for cosmetics and dolls since it has better transparency than polyvinyl chloride resin sheet and unstretched polypropylene sheet, and is also easy to treat after use.

[0003] In the manufacture of such cases, the sheet is cut to a prescribed shape, folded along a ruled folding line, bonded by means of applying adhesive to the overlapping parts to be bonded or by placing a small amount of adhesive between the overlapping parts to be bonded and the inner surface of the case, and finished to a prescribed case shape.

[0004]

[Problems That the Invention Is Intended to Solve] However, static electricity tends to be created on amorphous PET sheet, which causes dirt that adheres to the sheet surface to create whiskers during printing, or causes dirt to adhere to the case after assembly, thereby raising the problem of reduced product value. This adherence of dirt poses similar problems in thermoforming applications and the like. A method of kneading an antistatic agent with good heat resistance, such as an alkali metal salt of alkyl sulfonic acid or an alkali metal salt of alkyl benzenesulfonic acid, is generally used to improve the antistatic property of PET sheet. However, the antistatic effect will be inadequate if the amount added is within the range that enables the transparency of the sheet to be maintained. If a larger amount is added, the transparency will decline, and practical use as a transparent sheet becomes impossible.

[0005] Polyalkylene glycols have also been studied, but they have inadequate heat resistance, and are undesirable because their oxidative decomposition and pyrolysis lower the mechanical strength of the sheet and cause discoloration. Cationic antistatic agents have a strong antistatic effect, but pose problems in terms of food hygiene, and therefore cannot be used. Methods of applying an antistatic agent to the sheet surface have also been considered and are effective in improving the antistatic property, but have proven difficult in practice due to problems relates to the persistence of the effect, as well as to their printability and adhesive characteristics.

[0006] Another problem is the fact that the poor slip property of amorphous PET sheet leads to problems when feeding sheets to a printer when cases are to be worked, or other difficulties related to feeding. Moreover, once assembled the cases do not slide smoothly relative to each other, which poses a problem because the surfaces of the cases will tend to get scratched.

[0007]

[Means Used to Solve the Above-Mentioned Problems] The present invention provides a multilayered polyester sheet that has an excellent antistatic property without any loss in the sheet transparency, and in particular to a sheet that benefits from such excellent transparency and is suitable for use as a sheet that will yield a transparent case when folded along pre-formed ruled lines. Specifically, the main point of the present invention is a multilayered polyester sheet obtained by means of forming surface layers that comprise a composition that contains 0.05 to 2 parts by weight glycerin fatty acid ester per 100 parts by weight polyester resin on both surfaces of a transparent polyester resin base layer.

[0008] The present invention will be explained in detail below. The sheet of the present invention is a multilayered structure with surface layers comprising a glycerin fatty acid ester-containing polyester resin formed on both surfaces of a transparent polyester resin base layer. The base layer comprises a transparent polyester resin, and especially an ethylene terephthalate-based polyester resin. This layer is preferably not highly oriented and is in a substantially uncrystallized (amorphous) state to allow any secondary work such as folding and thermoforming.

[0009] Examples of the polyester resin of this base layer include an ethylene terephthalate homopolymer; a copolymer in which 60 mol% or more, and preferably 90 mol% or more, of the dicarboxylic acid component is terephthalic acid, and 60 mol% or more, and preferably 90 mol% or more, of the diol component is ethylene glycol; or a mixture of these polyester resins.

[0010] Examples of copolymer components include dicarboxylic acids such as isophthalic acid, phthalic acid, adipic acid, sebacic acid, and neopentyl acid; and diol components such as diethylene glycol, polyalkylene glycol, neopentyl glycol, and 1,4-cyclohexane dimethanol.

[0011] Ethylene terephthalate-based polyester resins are relatively inexpensive, easy to form into sheets, and have excellent strength, rigidity, transparency, and foldability. Polyethylene terephthalate (homopolymer), which is the most readily available, is an adequate base layer in many cases, and is also preferred in terms of its characteristics.

[0012] The polyester resin base layer has a transparency represented by a haze of 3% or less, and especially 2% or less. This transparency is easily obtained by means of admixing the polyester resin of the base layer with a trace amount (if any at all) of a lubricant, antistatic agent, or the

like that can eliminate transparency, and using sheet molding conditions that do not promote crystallization.

[0013] The polyester resin layers that serve as the surface layers of the sheet of the present invention comprise a glycerin fatty acid ester added to the polyester resin as an antistatic agent. Various polyester resins may be used as the polyester resin of the surface layers, including the same polyester resin as is used in the above base layer; however, the amorphous copolyesters discussed below are preferably used as sheets to be folded in consideration of their solvent adhesiveness.

[0014] Monoglycerides, acetylated monoglycerides, and the like are examples of glycerin fatty acid esters. However, such an ester is preferably resistant to pyrolysis and oxidative decomposition at 250 to 300°C, which is the molding temperature of the polyester resin. Monoglycerides are especially preferred in this regard. Examples of monoglycerides include glycerin monopalmitate, glycerin monostearate, glycerin monobehenate, and glycerin monocaprylate. Those that have undergone various modifications can also be used to improve the heat stability.

[0015] The amount of glycerin fatty acid ester added will vary to some extent depending on the type to be used. To prevent dirt from adhering to the sheet, its specific surface resistance (JIS K-6911) should be set to $1 \times 10^{16}\,\Omega$ or less, and especially to $1 \times 10^{15}\,\Omega$ or less. 0.05 parts by weight or more per 100 parts by weight polyester resin is sufficient to achieve these levels. Only a minimal antistatic property will be exhibited if the amount is less than 0.05 parts by weight. On the other hand, the transparency will decrease and the adhesiveness and printability adversely affected if the amount exceeds 2 parts by weight. Therefore, the preferred range is 0.05 to 2% by weight [sic], with a range of 0.3 to 0.5 parts by weight being especially preferred.

[0016] When the sheet of the present invention is used in folding work, an amorphous copolyester resin is preferably used as the polyester resin of the surface layers. The folded ends of the sheet will sometimes be bonded by solvents when cases are manufactured by means of folding. However, crystalline polyester resins will crystallize and whiten when contacted by a solvent. Therefore, having the surface layers constituted by an amorphous polyester resin permits good adhesion without any whitening being caused as a result of a widely used solvent such as tetrahydrofuran, cyclohexanone, ethyl acetate, and 1,1,2-trichloroethane.

[0017] The term "amorphous" means that the heat of crystallization (ΔHc) is 5 cal/g or less when the polyester resin or polyester resin mixture is cooled from a molten state at a rate of 10°C/min by a differential scanning calorimeter (Perkin Elmer DSC-7).

[0018] The amorphous copolyester resin may contain relatively large amounts of the copolymer components explained above as polyester resins for use in the aforementioned base layer. Concrete examples include amorphous copolyester resins consisting of a residue of a dicarboxylic acid that contains 20 to 40 mol% isophthalic acid, with the remainder being terephthalic acid, and a residue of a diol consisting mainly of ethylene glycol. This resin also has the advantage of being able to be procured somewhat inexpensively as an amorphous polyester resin.

[0019] Amorphous copolyester resin comprising a residue of a dicarboxylic acid consisting mainly of terephthalic acid, and a residue of a diol that contains 20 to 60 mol% 1,4-cyclohexane dimethanol, with the remainder being ethylene glycol, is also beneficially used.

[0020] These amorphous copolyester resins may also contain small quantities of components such as phthalic acid, adipic acid, sebacic acid, or another dicarboxylic acid, or a component such as propylene glycol, triethylene glycol, and diethylene glycol.

[0021] An especially preferred example of the latter is an amorphous copolyester resin comprising a residue of a dicarboxylic acid consisting mainly of terephthalic acid, and a residue of a diol that contains 20 to 60 mol% 1,4-cyclohexane dimethanol. Unstretched sheets of amorphous polyester made from PET and copolyester resins have suffered from embrittlement due to a decrease in impact strength when several months pass after the sheet has been manufactured. However, the aforementioned amorphous resin experiences little decline in strength over time, and reduction in strength and embrittlement of the sheet as a whole will be improved as a result of this resin being used in the surface layers. This amorphous resin is also superior to other amorphous copolyester resins in that it does not turn white when contacted by solvents.

[0022] The intrinsic viscosity of the polyester resins of the base layer and surface layers in the sheet of the present invention is preferably 0.5 or higher, and especially 0.6 or higher. The strength of the sheet will undesirably decrease when the intrinsic viscosity is less than 0.5.

[0023] There is no particular limitation as to the thickness of the sheet of the present invention. The appropriate thickness should be decided according to the application, and is usually

approximately 60 to 500 μm, an especially approximately 200 to 400 μm. The appropriate thickness of the polyester resin base layer therein may be decided according to the application, but is generally 50 to 400 μm; for example, foldable sheet is 150 μm or more, and preferably 200 to 400 μm, in thickness, and as described in the foregoing has a transparency represented by a haze of 3% or less, and especially 2% or less, within this range of thickness.

[0024] The thickness of the surface layers is generally about 5 to 50 μm per side in order to have a balance between the mechanical properties, such as the antistatic property and transparency. The balance can usually be attained by means of having a surface layer thickness (total of both sides) of about 15 to 30% of the total thickness of the sheet. When the sheet is used particularly in folding processes, having the thickness of the surface layers be 15 μm or more, and preferably 20 μm or more, will prevent whitening from occurring if the solvent penetrates through to the base layer.

[0025] Various additives such as stabilizers, lubricants, ultraviolet absorbers, pigments, and other thermoplastic resins can be added to the sheet of the present invention within ranges that do not adversely affect the transparency or other characteristics. Since the surface layers of the sheet of the present invention are generally thin, the addition of a lubricant that tends to harm the transparency to the surface layers may also improve the slip property without significantly affecting the transparency of the sheet.

[0026] Inert particles may be added to the surface layers if the slip property of the sheet is to be improved in this way. Examples of such inert particles include inorganic particles such as silica, titanium oxide, calcium carbonate, iron oxide, aluminum oxide, calcium oxide, and magnesium oxide and mixtures thereof; inorganic compounds such as talc and clay; and organic compounds such as high-melting point organic compounds and crosslinked polymers. The particles preferably have a high affinity with the polyester resin to prevent against any reduction in transparency. Silica particles are especially preferred in this regard. It is also effective to use organic lubricants such as fatty acid amides and various waxes in combination with these inert particles.

[0027] The aforementioned particles should have a mean particle diameter of 2 to 10 μm. Little improvement in the slip property will be realized if the particle diameter is less than 2 μm, because the irregularities formed on the sheet surface will be small. A diameter in excess of 10 μm will adversely affect the adhesiveness and printability of the sheet. A range of within 3 to

6 μm is especially suitable. The mean particle diameter of the particles is assumed to be the particle diameter at a cumulative weight fraction of 50% using a Coulter counter (made by Nihon Kagaku Kikai Co., Ltd.).

[0028] The amount of particles added should be 0.05 to 0.5 parts by weight, and especially 0.1 to 0.3 parts by weight, per 100 parts by weight of the polyester resin of the surface layers. An amount of less than 0.05 parts by weight will hardly improve the slip property. An amount of more than 0.5 parts by weight will decrease the transparency, adhesiveness, and other properties of the sheet.

[0029] A sheet surface roughness of 0.2 to 2 μm with regard to a 10-point mean surface roughness (Rz) stipulated by JIS B-0601 is generally preferred in order to achieve a balance between the slip property and the other characteristics. The surface roughness can be adjusted according to the amount of particles added and the particle diameter.

[0030] Sheet in which inert particles have been added to the surface layers can also be stretched at a low ratio to further improve the slip property of the sheet. The slip property can be improved by means of adding a relatively small amount of particles, because stretching will cause the inert particles to protrude from the sheet surface. Stretching is carried out at a ratio of 1.05 to 2 in at least one direction. Stretching will not improve the slip property if the draw ratio is less than 1.05. Stretching at a ratio of more than 2 will not substantially improve the slip property, and will also have an adverse effect on transparency, foldability, and secondary processability such as thermoformability. The preferred draw ratio is 1.1 to 1.6.

[0031] The stretching method involves stretching an unoriented multilayered sheet in a lengthwise direction, by means of creating a difference between the roll speeds, and in a widthwise direction if necessary, using a tenter. Stretching solely in a lengthwise direction is simple, and is preferred from a manufacturing cost standpoint. This stretching differs from ordinary stretching when used to strengthen the sheet in that the particles are used to form protuberances on the surface. Therefore, such stretching is preferably carried out under relatively high-temperature conditions, usually at 90 to 100°C.

[0032] The sheet of the present invention can be also obtained after each layer has been formed in advance by means of lamination using heat or an adhesive, but may also be obtained in practice by means of coextruding a molten multilayered sheet on a cooling drum using a feed block die or a multi-manifold die and rapidly cooling the extrudate. The resulting sheet will be

substantially unoriented and substantially amorphous. If stretched at a low ratio, the sheet will become substantially amorphous with low orientation.

[0033]

[Working Examples] The properties of the sheets were evaluated by means of the following methods in the working examples below.

[0034] 1) Haze: JIS K-7105

2) Friction coefficient: JIS K-7215

3) Specific surface resistance: JIS K-6911

4) Impact strength: Measured at a rate of 3 m/sec by a high-speed impact tester (made by Shimadzu Corporation; Hydroshot Impact Tester HTM-1).

[0035] (Working Example 1) A three-layered sheet that employed a copolyester (intrinsic viscosity: 0.8) with a diol component of 67 mol% ethylene glycol and 33 mol% 1,4-cyclohexane dimethanol, and a dicarboxylic acid [component] of terephthalic acid for the surface layers, and polyethylene terephthalate with an intrinsic viscosity of 0.65 for the base layer (core layer) was coextruded from a T-die at 285°C, and cast on a 40°C cooling drum to produce a three-layered sheet with two 25-μm surface layers and a base layer of 200 μm.

[0036] (A), (B), or (C) below were added to the surface layers as antistatic agents in the quantities shown in Table 1. The results obtained from evaluating the sheets are shown in Table 1.

[0037] (A) Glycerin monobehenate

(B) Modified glycerin monostearate

(C) Sodium alkyl sulfonate

[Table 1]

[Table 1]

No.	Antistatic agent		Specific surface resistance (Ω)	Haze (%)
	Type	Amount added (parts by weight)		
1	—	0	$>10^{17}$	1.3
2	A	0.1	5.3×10^{16}	1.4
3	A	0.3	2.3×10^{15}	1.5
4	A	0.5	5.4×10^{14}	1.5
5	B	0.03	8.6×10^{16}	1.4

No.	Antistatic agent		Specific surface resistance (Ω)	Haze (%)
	Type	Amount added (parts by weight)		
6	B	0.05	4.8×10^{16}	1.4
7	B	0.1	1.3×10^{16}	1.5
8	B	0.3	1.4×10^{14}	1.5
9	B	0.5	8.9×10^{13}	1.5
10	B	1.0	5.2×10^{13}	1.6
11	B	2.0	4.9×10^{13}	1.7
12	B	3.0	4.3×10^{13}	2.1
13	C	0.1	3.6×10^{16}	2.7
14	C	0.3	6.2×10^{11}	2.7

[0038] The sheets of the present invention, in which antistatic agents (A) and (B) had been added in the range of 0.05 to 2 parts by weight, had a specific surface resistance of 10^{16} Ω or less while maintaining good transparency. An optimum effect was achieved when the amount of antistatic agent was in the range of 0.3 to 0.5 parts by weight. Even though the transparency did not decrease to a great extent when the amount was in excess of 2.0 parts by weight (No. 12), a large amount of antistatic agent bled out onto the sheet surface, which became tacky as a result. The tackiness caused poor printability and blocking among other problems, and rendered practical use impossible. Sheets containing antistatic agent (C) exhibited a potent antistatic effect when a small amount was added, but suffered from a dramatic reduction in transparency.

[0039] (Working Example 2) Using the same polyethylene terephthalate as described in Working Example 1 as the base layer and polyester resins (a), (b), and (c) below in the surface layers, 0.3 parts by weight of modified glycerin monostearate and silica microparticles with a mean particle diameter of 2.5 μm were added to the surface layers in the quantities shown in Table 2. Unoriented three-layered sheets were then produced in the same manner as in Working Example 1.

[0040] These sheets were subsequently evaluated both in an unoriented state and after having been stretched in a lengthwise direction using a roll-type longitudinal stretching machine at 90°C in the ratios shown in Table 2. The final sheet thickness was 250 μm (the two surface layers were each 25 μm, and the base layer was 200 μm) in all cases.

[0041] (a) Polyethylene terephthalate (intrinsic viscosity: 0.65; ΔHc = 42 cal/g)

(b) Amorphous copolyester in which the diol was 67 mol% ethylene glycol and 33 mol% 1,4-cyclohexane dimethanol, and the dicarboxylic acid was terephthalic acid (intrinsic viscosity: 0.8, $\Delta Hc = 0$ cal/g)

(c) Amorphous copolyester in which the dicarboxylic acid was 78 mol% terephthalic acid and 22 mol% isophthalic acid, and the diol was ethylene glycol (intrinsic viscosity: 0.7; $\Delta Hc=0$ cal/g)

The results of evaluation are shown in Table 2.

[0042]

[Table 2]

[Table 2]

No.	Surface layer polyester	Amount of silica added (parts by weight)	Stretching multiple	Friction coefficient		Haze (%)
				μm	Md	
15	(a)	0	—	[could not be measured]		0.6
16		0.2	—	0.9	0.7	1.9
17		0.2	1.2	0.35	0.33	2.7
18	(b)	0	—	[could not be measured]		0.7
19		0.2	—	0.9	0.7	1.9
20		0.2	1.05	0.56	0.47	2.2
21		0.2	1.3	0.35	0.32	2.9
22		0.2	1.5	0.30	0.28	3.5
23		0.2	2.0	0.29	0.26	4.3
24		0.4	1.2	0.32	0.29	4.2
25		0.5	1.2	0.30	0.27	4.8
26	(c)	0	—	[could not be measured]		0.8
27		0.2	—	0.9	0.7	2.0
28		0.2	1.2	0.33	0.30	3.2

[0043] It is evident from these results that adding silica vastly improves the slip property of the sheet. Stretching slightly reduces the sheet transparency, but further improves its slip property. These sheets were assembled into cases by means of solvent bonding, in which a small amount of ethyl acetate was added to the parts to be bonded after the sheets had been punched and folded as shown in Figure 1. As a result, the sheets in which polyesters (b) and (c) had been used in the surface layers could be bonded firmly without any whitening. However, whitening occurred in the sheets in which polyester (a) had been used in the surface layers, which rendered such sheets

unsuitable for applications that involve solvent bonding. Furthermore, all of the sheets exhibited a specific surface resistance of approximately $10^{14}\ \Omega$, and a good antistatic property.

[0044] (Working Example 3) The impact strength values of Nos. 16, 19, 21, and 27, with which good results were obtained in Working Example 2, were measured both immediately after manufacture and after having been left to stand for two days at 50°C. The results are shown in Table 3.

[0045]

[Table 3]

[Table 3]

No.	Impact strength (kgf·mm)	
	Immediately after molding	After 2 days at 50°C
16	210	78
19	203	130
21	214	127
27	201	66

[0046] These results showed that the best initial strength and the best strength over time were exhibited by those products (Nos. 19 and 21) in which the aforementioned polyester (b) had been used as the polyester resin in the surface layers.

[0047]

[Effect of the Invention] The sheet of the present invention contains a glycerin fatty acid ester as an antistatic agent in thin surface layers, thereby affording an excellent antistatic property without any transparency being lost, and enabling the sheet to be suitably used in folding and in a variety of other applications.